



Novel Biomaterials for Packaging Applications

Anjali Bajpai¹, Vidhya Raj²

Professor, Department of Chemistry, Govt. Science College, Jabalpur, India¹

Research Scholar, Department of Chemistry, Govt. Science College, Jabalpur, India²

Abstract: Guar gum was hydrophobically modified by condensation with dimer acid by microwave irradiation; the resulting product was used to prepare a film by mixing with poly vinyl alcohol. The preparation of condensation product and the film was optimized by variation of various reaction parameters. Products were characterized by FTIR spectroscopy, SEM, viscosity, tensile strength and permeability measurements. The application of films for food packaging is suggested on the basis of various properties and biodegradation in moist soil.

Keywords: Guar gum, dimer acid, hydrophobically modified guar gum, poly vinyl alcohol, biodegradation.

I. INTRODUCTION

The fabrication of barrier packaging films has gained significant momentum in recent years [1]. Food packaging is not only used as a container but also acts as a protective barrier with some innovative functions such as to hinder gain or loss of moisture, prevent microbial contamination and act as a barrier against permeation of water vapour, oxygen, carbon dioxide and other volatile compounds such as flavors and taints in addition to the basic properties of packaging materials such as mechanical, optical, and thermal properties [2]. The production and use of non-biodegradable materials or plastics derived from petroleum products as food packaging materials have significantly increased, which causes the problem in waste disposal. There is an increasing demand towards development of food packaging materials or bioplastics that could rapidly degrade and completely mineralize in environment. However, the use of biopolymers as food packaging materials has drawbacks such as poorer mechanical, thermal, and barrier properties. Hence research efforts are being focussed to improve the properties of the biopolymers [3].

Nano-sized fillers, could bring a large range of improved properties (stiffness, permeability, crystallinity, thermal stability) to extend applications of biopolymers. A review was dedicated to this novel class of materials based on clays 'nano-biocomposites' [4]. Nano-particles such as clay can be used in thermoplastic starch (TPS) polymer matrices to overcome their disadvantages [5-7]. There is a great rush for nanotechnology these days, however, the disadvantages or long term effects of nanomaterials are still to unravel.

Guar gum (GG) can be a potential candidate for production of bioplastics because of its long polymeric chain, high molecular weight and wide availability. India accounts for 80% of world production of GG. GG is a non-ionic edible polysaccharide found abundantly in nature and is a cold water swelling polymer. It has a wide variety of non-food and food uses.

It is used as a stiffener in ice cream, yogurt, bakery and soups; as a stabilizer for cheeses, puddings and cream; and as a meat binder. GG is used as a viscosity builder and water binder in many industries, viz. explosives, foods, cosmetics and pharmaceuticals, mining, tobacco, textiles, pulp and paper. It has many properties desirable for drug delivery applications. However, due to its high swelling characteristics in aqueous solution, the use of GG as delivery carriers is limited. Guar gum can be modified by derivatization, grafting and network formation to improve its property profile for a wide spectrum of biomedical applications. Guar samples were derivatized with hydroxypropyl, N-alkylamide, and carboxyl moieties [13]. The hydrophobic long chain alkyl (C14) was successfully grafted onto guar gum [14], hydrophobically modified guar gum was developed as thickener [15].

Hydrophobically modified starches are known for their suitability in biomedical applications, because in the aqueous phase, the hydrophobic cores of polymeric nanoparticles are surrounded by hydrophilic outer shells. Thus the inner core can serve as a nano-container for hydrophobic drugs [8, 9]. Also, hydrophobically modified polysaccharides are emerging as novel carriers of drugs, because of their controlled solubility and biocompatibility in vivo. In addition, their improved properties as compared to original starch could be used as a thickener or an emulsifier [10-12].

However, little attention has been focussed towards the application of hydrophobically modified polysaccharides as packaging materials. This modification is expected to reduce the hydrophilicity. The formation of physical crosslinks through hydrophobic domains would enhance the film forming property. With this view the present paper reports hydrophobic modification of guar gum was by condensation with dimer acid (C36) which is derived from castor oil, a renewable resource.



II. EXPERIMENTAL

A. Preparation of Hydrophobically Modified Guar Gum (HMGG)

The emulsions of Dimer acid in 10% NaOH were thoroughly mixed with finely powdered Guar Gum, and then PTSA and DBSA were added. The homogenous reaction mixture was obtained by stirring magnetically; it was finally irradiated in a domestic Kenstar microwave oven. The resulting mass was thoroughly dried in a hot air oven.

B. Preparation of Film from HMGG

1g of HMGG was mixed with 10 of mL of Millipore water and kept overnight. HMGG swelled into a gel like material, it was thoroughly mixed with 2 mL of 6.7% aqueous solution of polyvinyl alcohol (PVA), 2 mL of 0.2 N HCl, 1 mL of glycerol, 1 mL glutaraldehyde and 20 mL water and then heated in a hot air oven at 60 °C for 5 hours in a Petri dish. The film obtained on evaporation of water was carefully washed with water to remove adhered chemicals and dried again in the hot air oven.

C. Measurements

The FTIR spectra of various samples were recorded on a SHIMADZU 8400-S FTIR spectrophotometer in 4000-500 cm^{-1} range as DRS in KBr dispersion. The permeability of the hybrid film was determined for some selected solvents by the procedure described by Bajpai and Bajpai [16]. The kinetic course of permeability for some selected solvent vapours was followed. 5 mL of solvent was taken in a test tube (capacity 15 mL) and its mouth was sealed with the polymeric film by an adhesive in such a manner that adhesive did not come in direct contact with the solvent vapour. This boiling tube was weighed initially and then at various time intervals with a precision balance to follow the weight loss of the solvent due to permeability.

The thicknesses of various films were measured by a screw gauge. Tensile strength of a film with thickness 0.264 mm was measured by Universal testing machine with 1 N load using a piece 25 mm long and 10 mm wide.

III. RESULTS AND DISCUSSION

Guar gum was hydrophobically modified by condensation with dimer acid (having 36 carbon atoms), which is a dimer obtained by Diels-Alder cycloaddition reaction of ricinoleic acid, derived from castor oil, a renewable resource. Guar gum is found in the seeds of leguminous plants like cyanmopsis tetragonolobous and psoraloids. Guar is a galactomannan that consists of a straight chain of mannose units joined by β -D linkages having an α -D-galactopyranose units attached to this linear chain by 1,6-linkages.

In pure polysaccharide guar, the ratio of D-galactose to D-mannose units is 1:2. The molecular weight of guar is approximately 2.2×10^5 . The structure of guar gum is shown in Fig. 1 and that of dimer acid in Fig. 2.

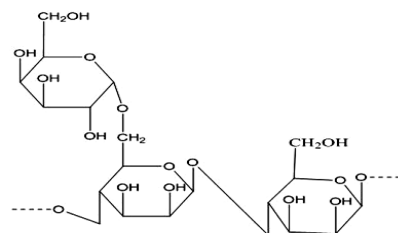


Fig.1. Structure of guar gum

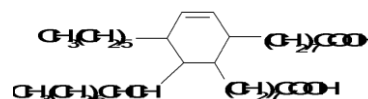


Fig.2. Structure of dimer acid

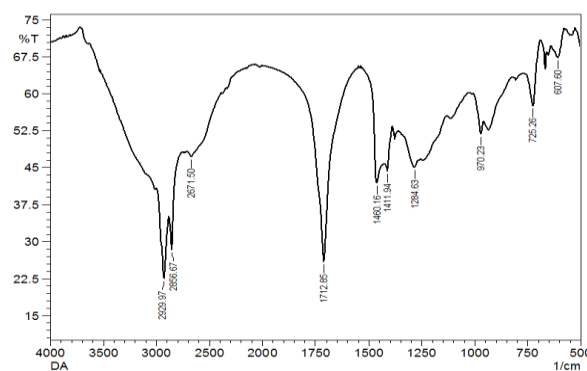


Fig.3. FTIR spectrum of Dimer Acid

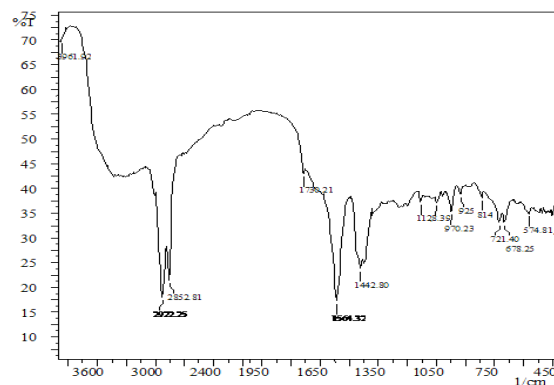


Fig.4. FTIR spectrum of HMGG

TABLE I EFFECT OF VARIATION OF VARIOUS INGREDIENTS ON THE PROPERTIES OF FILMS PREPARED FROM HMGG

Ingredients	Sample codes*			
	A	B	C	D
HMGG (g)	1	1	1	1
PVA 6.7% aqueous solution (mL)	2	-	2	2
HCl 2N aqueous solution (mL)	2	2	-	2
Glutaraldehyde 25% aqueous solution (mL)	1	1	1	-
Glycerol (mL)	-	1	1	1

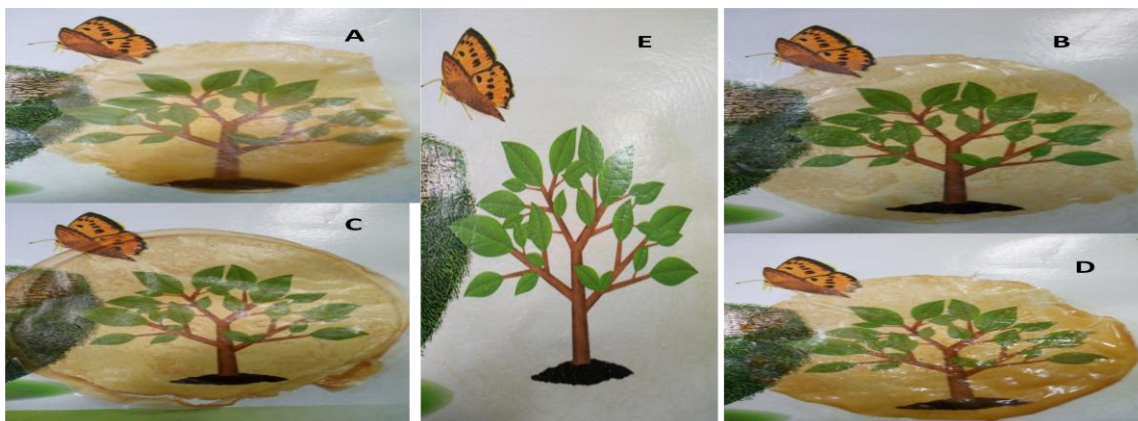


Fig.5. Images depicting the transparency of films prepared by variation of constituents: see Table I for description of codes A, B, C and D, E– Original picture

* A- Non-sticky, rough surface, brittle, transparent, yellow coloured film

B-Shining, flexible, elastic, transparent, pale yellow coloured film

C- Shinning, flexible, limited stretchability, transparent, yellow brown coloured film

D- Sticky, stretchable, yellow coloured film

The films were transparent and glossy. This is probably a manifestation of the formation of highly ordered structures called microphase separated structures (MSS). Since the dimensions of MSS lies in the range of gyration radius of the molecules these nanostructured heterogeneous polymeric materials were transparent [17]. Elongation at break was found to be 59 mm, percent elongation 236.0% and breaking strength 0.1 N/mm.

A perusal of FTIR spectra of dimer acid and HMGG these spectra clearly evinced the significant extent of condensation reaction. The enhanced intensities of symmetric and asymmetric CH_2 stretching bands at 2852 and 2922 cm^{-1} respectively in FTIR spectrum of HMGG suggested that the intensity of broad envelope like band from carboxylic acid groups decreased appreciably.

The broad band in 2500-3600 cm^{-1} range seemed to originate from the residual OH groups of guar gum. The strong band at 1726 cm^{-1} ascribed to the carbonyl stretch in the spectrum of dimer acid reduced as a shoulder on a broad band at 1564 cm^{-1} . Appearance of a band at 1730 cm^{-1} was a clear indication of formation of ester linkages between guar gum and dimer acid.

D. Scanning electron microscopy (SEM)

Analysis of scanning electron micrographs suggested that when DA and GG were in 1:1 proportion in condensation product (HMGG-5) the film appeared homogeneous in SEM with no phase separation. However, when proportion of GG was increased, i.e. DA and GG in 1:2 ratio, then self assembled hydrophobic domains appeared as dark spots and the surface of the film was rough.

The films were prepared in aqueous medium, hence it was inferred that hydrophobic domains of DA residues assembled in the inner core. Hydrophilic GG residues occupied the outer surface along with PVA and glycerol

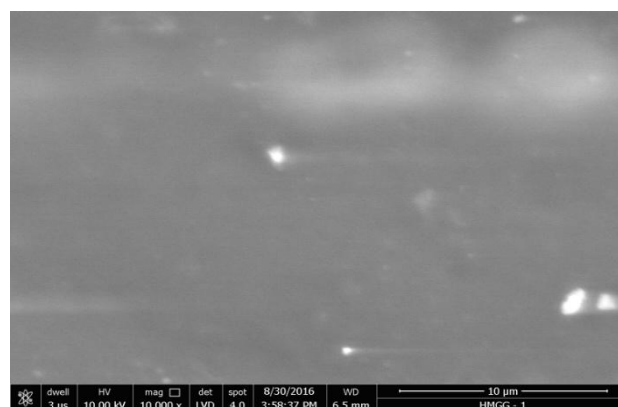


Fig. 6 -Scanning electron micrograph of film prepared from HMGG-1 (ratio of dimer acid and guar gum 1:2)

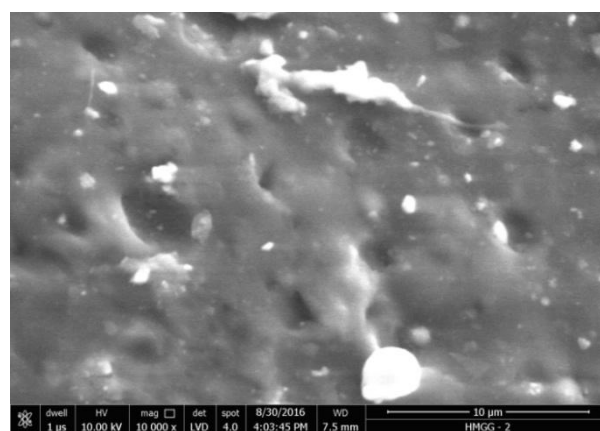


Fig. 7- Scanning electron micrograph of film prepared from HMGG-2 (ratio of dimer acid and guar gum 1:1)

Which were used as the plasticisers. Because this film from HMGG-2 was smooth, homogeneous and transparent, further studies were carried out on this film.



E. Permeability measurements in various solvents
The results of permeability measurements in various solvents are depicted in Fig. 8. It is apparent that as compared to other solvents, rate of permeation was high for acetone and methanol, which are polar as well as more volatile. Initial rate for ethanol was highest, however, it diminished steeply and values became negative due to moisture absorption from the atmosphere. Negative values were observed for DMSO and DMF also which are hygroscopic solvents.

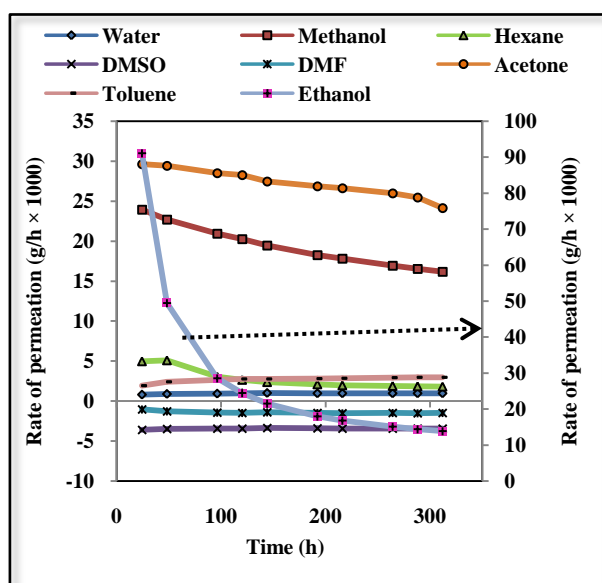


Fig. 8. Permeability measurements in various solvents

On a perusal of the results of permeation studies and correlations based on solubility parameter of solvent (δ_s) and Hydrogen Bonding Index (HBI), it was inferred that permeation of the solvents involved interaction with the hydrophobic and hydrophilic domains of the film. However, small values of permeation rates suggested that hydrophobic modification of GG was successful in reduction of its strong hydrophilic character. Further, the permeation of hydrophobic solvents was also restricted.

F. Thermal Stability

The film was heated in a muffle furnace for 5 hours at 105 °C and 67.62% of weight was lost but film was still intact. It became harder, the surface turned rough and dark brown in colour.

G. Biodegradation study

The experiments of permeation studies were carried out in rainy season and the experimental setup was not kept in any isolated chamber, but no fungal growth was observed even in a month's time. This showed that the films have sufficient shelf life for packaging application. A piece of film was kept in soil which was being moistened intermittently. Initially the film became slimy, then swelled and appeared white in colour due formation of

crazes (Fig. 9 c). Crazes appear due to a fine network of cracks but the surfaces of the crazes are connected by oriented polymeric structures, and a completely crazed specimen can continue to sustain appreciable stresses without failure [18]. The film degraded almost completely in two months (Fig. 9 d).

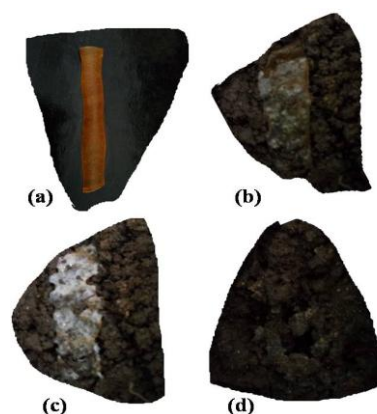


Fig. 9. Biodegradation of HMGG film in soil (a) Original film against black background. Degradation of film in moist soil after (b) 2 hours, (C) 05 days, (d) 2 months.

IV. CONCLUSION

A novel biopolymer based material or biomaterial HMGG was developed microwave irradiation of aqueous emulsions of guar gum and dimer acid, both of which are derived from renewable resources. The films prepared from HMGG exhibited sufficient tensile strength and flexibility required for packaging. Low permeation rate for water and other solvents suggested use for food items with short shelf lives, such as fresh vegetables. The "Green" material (produced by green chemistry) can be composted after its use for biodegradation in soil.

ACKNOWLEDGMENT

Authors are thankful to Sophisticated Instrumentation centre for applied research and testing (SICART), Ahmedabad Gujrat, for SEM analysis. Vidya Raj is thankful to UGC, New Delhi for financial support in form of RGNF.

REFERENCES

- [1] A.A. Gokhale, I. Lee, "Recent advances in the fabrication of nanostructured barrier films," *Journal of Nanoscience and Nanotechnology*, vol.14 (3), pp. 2157-2177, 2014.
- [2] J. W. Rhim, H. M. Park, C. S. Ha, "Bio-nanocomposites for food packaging applications," *Progress in Polymer Science* vol. 38, pp. 1629– 1652, 2013.
- [3] S. H. Othman, "Bio-nanocomposite Materials for Food Packaging Applications," *Agriculture and Agricultural Science Procedia*, vol. 2, pp. 296 – 303, 2014.
- [4] P. Bordes, E. Pollet, L. Avérous, "Nano-biocomposites: Biodegradable polyester/nanoclay systems," *Progress in Polymer Science (Oxford)*, vol. 34 (2), pp. 125-155, 2009.



- [5] A.M. Nafchi, M. Moradpour, M. Saeidi, A. K. Alias "Thermoplastic starches: Properties, challenges, and prospects" *Starch/ Stärke*, vol. 65 (1-2), pp. 61-72, 2013.
- [6] D. K. M. Matsuda, A. E. S. Verceheze, G. M. Carvalho, F. Yamashita, S. Mali "Baked foams of cassava starch and organically modified nanoclays," *Industrial Crops and Products*, vol. 44, pp.705- 711, 2013.
- [7] M. M. Reddy, S. Vivekanandhan, M. Misra, S. K. Bhatia, A. K. Mohanty, "Biobased plastics and bionanocomposites: Current status and future opportunities," *Progress in Polymer Science*, vol. 38, pp.1653- 1689, 2013.
- [8] H. Namazi and A. Kanani, "Investigation diffusion mechanism of β -lactam conjugated telechelic polymers of PEG and β -cyclodextrin as the new nanosized drug carrier devices," *Carbohydr. Polym.*, vol. 76, pp. 46-50, 2009.
- [9] J. H. Kim, Y. S. Kim, S. Kim, J. H. Park and I. C. Kwon, "Hydrophobically modified glycol chitosan nanoparticles as carrier for Paclitaxel," *J. Control. Release*, vol. 111, pp. 228-234, 2006.
- [10] M. J. Alonso, A. Sanches, S. Wadhawan, R. Kaushik, R. Kumaria, and K. Nansal, "Chitosan microspheres as a potential carrier for drugs," *Int. J. Pharm.*, vol. 274, pp. 1-33, 2004.
- [11] B. VanVeen, J. Pajander, K. Zuurman, R. Lappalainen, A. Poso, H.W. Frijlink, and J. Ketolainen, "the effect of powder blend and tablet structure on drug release mechanisms of hydrophobic starch acetate matrix tablets," *Eur. J. Pharm. Biopharm.*, vol. 61, pp. 149-157, 2005.
- [12] L. Qiao, Q. Gu, and H.N Cheng, "Enzyme-catalyzed synthesis of hydrophobically modified starch," *Carbohydr. Polym.*, vol. 66, pp. 135-140, 2006.
- [13] U. D. N. Bajpai, A. K. Bajpai, "Kinetic behaviour of permeability of polyethylene membrane to chloroform vapour," *Polym. Int.*, vol. 31, pp.127-130, 1993.
- [14] F. J. Baltá-Calleja, M. E. Cagiao, R. Adhikari, G.H. Michler, "Relating microhardness to morphology in styrene/butadiene block copolymer/polystyrene blends," *Polymer*, vol. 45, pp.247-254, 2004.
- [15] R. Mafi, R. Pelton, Y. Cui, H. Ketelson, "Weak gelation of hydrophobic guar by albumin in simulated human tear solutions," *Biomacromolecules*, vol.15 (12), pp. 4637-4642, 2014.
- [16] F. Chen, X.G. Wang, R.S. Yang, "Synthesis and characterization of hydrophobic modification guar gum," *Advanced Materials Research*, vol.952, pp. 121-124, 2014.
- [17] J. Zhao, Y. Shen, L. Wang, X. Lai, "Synthesis of hydrophobic modified guar gum thickener and correlation analysis of its structure and property," *Polymeric Materials Science and Engineering*, vol.27 (10), pp. 58-61, 2011.
- [18] A. Bajpai, N. Dixit "Synthesis and Characterization of a Film-Forming, Crosslinked, Amphiphilic Block Copolymer of Butadiene and Acrylamide," *Journal of Polymer Science*, vol. 44, pp. 3290-3303, 2006.



Vidhya Raj was born in Damoh, India, and received her B.Sc., M.Sc. and M. Phil. degrees from Rani Durgavati University, Jabalpur in 2010, 2012 and 2013, respectively. She is Pursuing Ph. D. degree in Chemistry at the Government Science College, Jabalpur under the supervision of Professor Anjali Bajpai in the field of polymer chemistry. Her research interests include green chemistry, polymer synthesis and characterization.

BIOGRAPHIES



Anjali Bajpai was born in Jabalpur, India, and received her B.Sc. and M.Sc. degrees from Government Science College, Jabalpur, affiliated to Jabalpur University, Jabalpur in 1975 and 1977, respectively. She earned her Ph.D. degree in Chemistry in 1983 at the Rani Durgavati University, Jabalpur under the supervision of Professor D. D. Mishra in the field of coordination chemistry. She accepted an Assistant Professor position at Government Science College, Jabalpur in 1984. She has worked on organometallic chemistry as a visiting professor at Osaka City University, Osaka, Japan. She became Professor in 2006. Her research